



Figure 1a. A general mixture synthesis with fluorous tags using a mixture of tagged compounds.

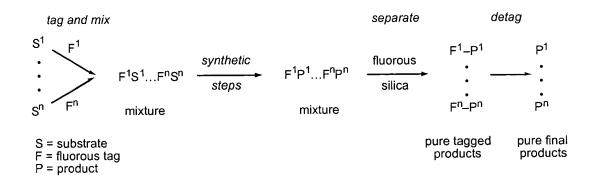


Figure 1b. A general mixture synthesis with fluorous tags using a mixture of tagged compounds and a mixture of reactants.

$$F^{1}S^{1}R^{1}...F^{1}S^{1}R^{0}$$

$$F^{1}S^{1}...F^{n}-S^{n}$$

$$R^{1}-R^{0}$$

$$R^{1}-R$$

Figure 1c. A general mixture synthesis with fluorous tags using fluorous tagged reactants and a substrate.

Figure 2. A representative example of a synthesis with a mixture of flourous tagged compounds and a mixture of reactants

3 libraries of 12 products, see below

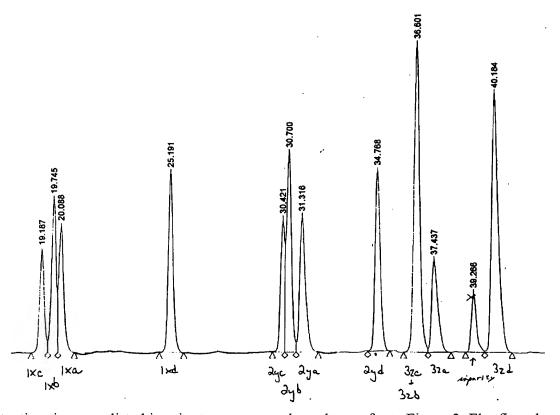
			Library	Esters	Products in order of retention times (min) on Fluofix column
Tags R ^f	Esters	Thiols	1	1x, 2y, 3z	1xc (18.5); 1xb (18.9); 1xa (19.3); 1xd (23.8); 2yc (28.7); 2yb (28.7); 2ya (29.5); 2yd (32.6); 3zc (34.1); 3zb (34.1); 3za (35.1); 3zd (37.9)
x C6F13 y C8F17 z C10F21	1 Me H 2 Pr H 3 H Me	a C ₆ H ₅ b 2-naphthyl c p-MeOC ₆ H ₄ d p-BuC ₆ H ₄	2	1y, 2z, 3x	3xc (18.1); 3xb (18.5); 3xa (18.7); 3xd (23.4); 1yc (27.0); 1yb (27.0); 1yc (27.6); 1yd (31.2); 2zc (35.6); 2zb (35.6); 2za (36.5); 2zd (38.8)
			3	1z, 2x, 3y	2xc (20.4); 2xb (20.9); 2xa (21.0); 2xd (25.3); 3yc (26.4); 3yb (26.4); 3ya (27.0); 3yd (30.8); 1zc (34.2); 1zb (34.2); 1za (35.1); 1zd (37.8)

APPROVED O.G. FIG.

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Figure 3. A representative HPLC trace of a library of compounds produced in the synthesis of Figure 2.^a



a) Retention times are listed in minutes; compound numbers refer to Figure 2; Fluofix column eluting with a gradient of 80% methanol/water increased to 100% methanol over 40 min. The peak at 39 min is an unknown impurity.

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Figure 4. Preparation of Precursors for a Mixture Synthesis of Mappicine Analogs

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Figure 5. Mappicine Mixture Synthesis and Separation

Individual, pure samples of 6a,e

Mixture of 5a-e

separate on Fluofix™

Mixture of protected mappicines 6a-e

Retention Time Yield Time Gradient 36% 0-5 min 80% MeOH/H₂Oа 3 min 41% 29% 5-25 min 90% MeOH/H₂O b 13 min >25 min 18 min 100% MeOH C ď 36% 21 min 28 min 43%

* * ~ * * * * * *

Figure 6. Preparation of precursors for a mixture synthesis of mappicine analogs (Example 8)

OMe CHO Et₃SiH
$$\frac{1}{BF_3 \cdot OEt_2, 60 \, ^{\circ}C}$$
 TMS $\frac{1}{I}$ $\frac{1}{I}$

4a
$$R^2 = CH_2Ph$$
, $R^1 = {}^tBuMe_2Si$, 79%
4b $R^2 = Et$, $R^1 = H$, 86%
4c $R^2 = {}^tBu$, $R^1 = H$, 68%
4d $R^2 = CH_2Ph$, $R^1 = H$, 62%

4d
$$R^2 = CH_2Ph$$
, $R^1 = H$, 62%
4e $R^2 = Et$, $R^1 = Ph$. 69%

He
$$R^2 = \text{Et}$$
, $R^1 = Ph$, 69%